446. *The Micro-flame Detector in Gas–Liquid Partition Chromatography: Correlation of Response with Heats of Combustion.*

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Gas–liquid partition chromatography is carried out with nitrogen or carbon dioxide as carrier gas. Hydrogen is added to the gas stream as it emerges from the column, and the resultant mixture burnt in a draught-free housing in contact with a thermocouple. The temperature rise of the thermocouple during the combustion of any band is found to be directly proportional to the rate of liberation of heat in the combustion of the band.

RECENTLY a novel method of detection for use in gas–liquid partition chromatography has been described by Scott [1] in which hydrogen is used as carrier gas and is burnt at a jet at the outlet of the column. By measuring the changes in the temperature of a thermocouple placed in the flame, the elution of various bands can be observed as peaks on a temperature–time plot. It appeared to us that a direct correlation should exist between the areas of such peaks and the heats of combustion of the substances which gave rise to them. Using a simple apparatus, we have in fact been able to show that a good linear relation exists between the peak area per mole of some 24 organic substances and their molar heats of combustion. As a result of the work we have also concluded that the micro-flame detector has approximately the same sensitivity as the more widely used thermal conductivity type and that it is considerably less temperamental at high sensitivity.

The method originally described suffered from the disadvantage that during the elution of a band the basic thermocouple temperature rose in the direction of higher temperature. This effect, which renders quantitative results unreliable, is apparently due to a slight increase in the hydrogen flow rate as the band emerges from the column, the band acting as a viscous plug when within the column. This disadvantage has been overcome by Wirth,[2] who uses, instead of hydrogen, an inert carrier gas such as nitrogen or carbon

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[1] Scott, *Nature*, 1955, **176**, 973.

[2] Wirth, personal communication.

dioxide. The hydrogen is passed through a separate column and mixed with the carrier gas immediately before combustion. In this way a constant flow of hydrogen is ensured irrespective of what may pass through the chromatography column proper. This modification of the original design has been found to be completely satisfactory in removing base line steps and has no detrimental effect on the stability or sensitivity of the apparatus.

The greatest difficulty in construction of the micro-flame detector lies in ensuring an absolutely stable flame when no foreign gas is passing through the flame. In order that the apparatus used in the present work should be able to measure a heat output of 0·5 cal./min. with an accuracy of 1% (this corresponds roughly to the maximum rate of heat liberation during the elution of 100 μg. of benzene under our experimental conditions), a flame stable to ±0·01° at an ambient temperature of 600—800° is required. The flow of hydrogen must therefore be stabilised to about 1 part in 10^5 and the flame itself must be mounted in an absolutely draught-free housing. In our apparatus the flow rate was stabilised by passing the hydrogen, kept at a pressure of some 20 cm. Hg above atmospheric by a water bubbler, through a series of six stabilising vessels each consisting of a length of fine capillary leading into a volume of about 20 c.c. The hydrogen was then passed through a " dummy " chromatographic column before being mixed with the carbon dioxide or nitrogen which was used as carrier gas for the chromatography proper. The flow of the carrier gas was similarly stabilised by two stabilising vessels.

The prevention of draughts was ensured by mounting the jet inside an asbestos pipe, 50 cm. long and 10 cm. in diameter, lined with five spaced concentric layers of fine copper gauze. The jet itself was made of quartz and had a diameter of 0·2 mm. The thermocouple was mounted about 1 cm. above the jet and was contained in a very thin-walled quartz capillary which served to minimise corrosion and prevented any catalysis of the combustion. The output of the thermocouple was balanced by means of a potentiometer and the off-balance e.m.f. supplied to a sensitive galvanometer. With this arrangement a flame stability of ±0·03° was achieved. We were therefore in a position to analyse mixtures containing quantities of the order of 300 μg., but in practice, owing to the difficulty of adding such minute amounts of liquids, samples of the order of 2—5 mg. were used. The thermocouple used in the experiments was of platinum–platinum-13% rhodium which gave a deflection of 3 cm./°c with the galvanometer employed. Random fluctuations were of the order of 1 mm. The chromatography column was 100 cm. long, 8 mm. in diameter, and was packed with a 3 : 2 mixture of Celite 545 and Silicone oil D.C. 500. The column temperature was 65°, and the flow rates of hydrogen and carbon dioxide (used throughout the experiments as carrier gas) were 100 and 66 c.c./min., respectively. The basic thermocouple temperature with these flow rates was 650° above room temperature.

Before commencing experiments on the relation between the heats of combustion of various substances and the sensitivity of the micro-flame detector it was necessary to confirm that the response of the detector was a linear function of the amount of any component passed. Since it is extremely difficult to add accurately very small amounts of liquids, a number of mixtures of different compositions were made up with acetone and benzene. A logarithmic plot of the relative peak areas against the relative amounts of the two components is shown in Fig. 1. The line, which has been drawn with unit gradient, passes within experimental error through all the points and confirms that the response is in fact linear. More extended experiments by Wirth have led to the same conclusions.

In correlating peak areas with the heats of combustion, an analogous method was used. Solutions of a variety of substances were made up in toluene by accurate weighing, and 2—5 mg. of each mixture used for chromatography, the mixtures being injected into the column by means of a hypodermic syringe through a serum cap. The peak areas were then measured, and the peak areas per mole calculated relative to a value of 100 for toluene. These values are plotted in Fig. 2 against the heats of combustion per mole of the various substances. The heat of combustion values are those for 25°; no correction has been made for the temperature of the flame since other sources of error are probably greater and the correction term would in any case be roughly proportional to the heats of combustion for any series of compounds. The results all fall on a good straight line and therefore establish that the heat of combustion is the major factor influencing the sensitivity of the micro-flame detector. Changes in the shape of the flame appear to have only a secondary effect on the response.

In order to obtain an absolute calibration of the instrument some experiments were carried out with a 1 : 5 (v/v) solution of benzene in carbon tetrachloride. Using about 6 µl. of the mixture we were thus able to inject with reasonable accuracy about 1 µl. of benzene. In this way reproducibility of the order of 5% was obtainable for the benzene peak area over several experiments and a rough value for the sensitivity of the detector per calorie was obtained.

With a hydrogen flow of 100 c.c./min. the basic rate of heat production by the flame is 240 cal./min.; 0·88 mg. of benzene, which has a heat of combustion of 8·8 cal., gave a peak of mean area 19·2° min., with a maximum temperature rise during elution of 11·2°. The rise in flame temperature for an excess heat production at the rate of 1 cal./min. is therefore :

FIG. 1. *Linearity of response of detector to mixtures of different compositions.*

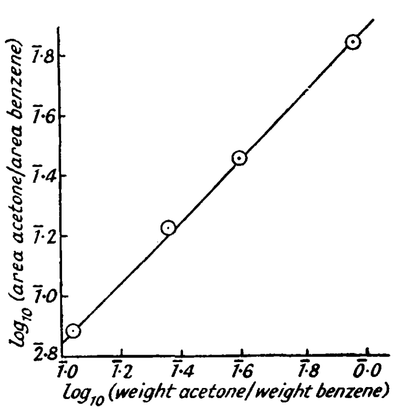

FIG. 2. *Variation of sensitivity of flame detector with heat of combustion of various substances.*

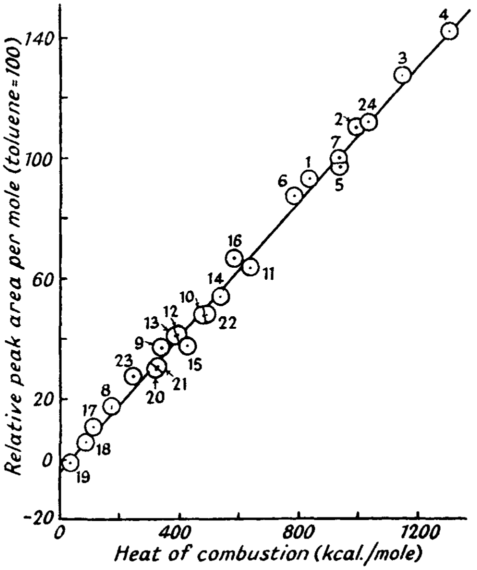

FIG. 2.

(1) *n*-Pentane; (2) *n*-hexane; (3) *n*-heptane; (4) *n*-octane; (5) *cyclo*hexane; (6) benzene; (7) toluene; (8) methyl alcohol; (9) ethyl alcohol; (10) *n*-propyl alcohol; (11) *n*-butyl alcohol; (12) ethyl formate; (13) methyl acetate; (14) ethyl acetate; (15) acetone; (16) ethyl methyl ketone; (17) methylene chloride; (18) chloroform; (19) carbon tetrachloride; (20) ethyl chloride; (21) ethyl bromide; (22) *iso*propyl bromide; (23) carbon disulphide; (24) triethylamine.

$$\Delta T = 19{\cdot}2/8{\cdot}8 = 2{\cdot}18^\circ \text{ min. cal.}^{-1}$$

Extrapolation of this value to a rate of heat production equal to that of the hydrogen flame itself gives a temperature rise of 520°. This value may be compared with the actual basic thermocouple temperature of 650°. A very rough estimate of the sensitivity of the micro-flame detector can thus be made on the assumption that the temperature of the thermocouple above room temperature is directly proportional to the heat liberated in the flame. Alternatively, if T is the thermocouple temperature and Q the heat liberated in the flame, the temperature increase δT due to an excess heat production δQ is given by $\delta T = \delta Q \times aT/Q$, where a is a constant close to unity, in our case 0·80.

The results which have been described emphasise a number of useful points regarding the micro-flame detector in gas–liquid partition chromatography. This detector has a sensitivity of the same order as that of the thermal conductivity detector but it is considerably simpler to construct and less troublesome in action. It responds to various substances according to their heats of combustion rather than to the number of moles in the sample. The method is therefore particularly suitable for the analysis of compounds of high molecular weight. While the thermal conductivity detector has roughly the same sensitivity per mole for any homologous series, the micro-flame detector has roughly the same sensitivity per g. The thermal conductivity detector should therefore be employed in the analysis of permanent gases, non-combustibles, and substances of low heats of combustion (nitrogen, oxygen, rare gases, hydrogen, methane, ethane, carbon tetrachloride, chloroform, etc.), while the micro-flame detector is the more suitable in the analysis of mixtures containing substances of higher molecular weights and higher heats of combustion such as those found in petroleum distillates.

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